Exploratory Studies of Novel Sodium-ion Battery Systems

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BAT287

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Relevance and Project Objectives

✓ *To increase the energy density, searching for new cathode materials for Na-ion batteries.*

- Using *in situ* and *ex situ* XRD and hard X-ray absorption (hXAS) to study new low-cost P2-type iron based cathode materials ($Na_{0.7}[Cu_{0.15}Fe_{0.3}Mn_{0.55}]O_{2)}$ for sodium-ion batteries during charge-discharge cycling.
- Using soft X-ray absorption (sXAS) to study $Na_{0.7}[Cu_{0.15}Fe_{0.3}Mn_{0.55}]O_2$ and $Na_{0.7}[Cu_{0.2}Fe_{0.2}Mn_{0.6}]O_2$ electrode materials at different SOCs at Fe L-edge, Cu L-edge, and oxygen K-edge.
- Using *In situ* XRD to study new stabilized global P2 phase cathode material $Na_{0.72}[Li_{0.24}Mn_{0.76}]O_2$ for sodium-ion batteries during charge-discharge cycling.

✓ *Diagnostics study aimed to improve the calendar and cycle life of batteries.*

- to develop in situ diagnostic techniques with surface and bulk sensitivity to improve the calendar and cycle life of sodium batteries by studying the mechanism of capacity and power fading of Na-ion and Na metal batteries.

✓ *Diagnostics study of electrode materials with lower cost potential.*

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Milestones

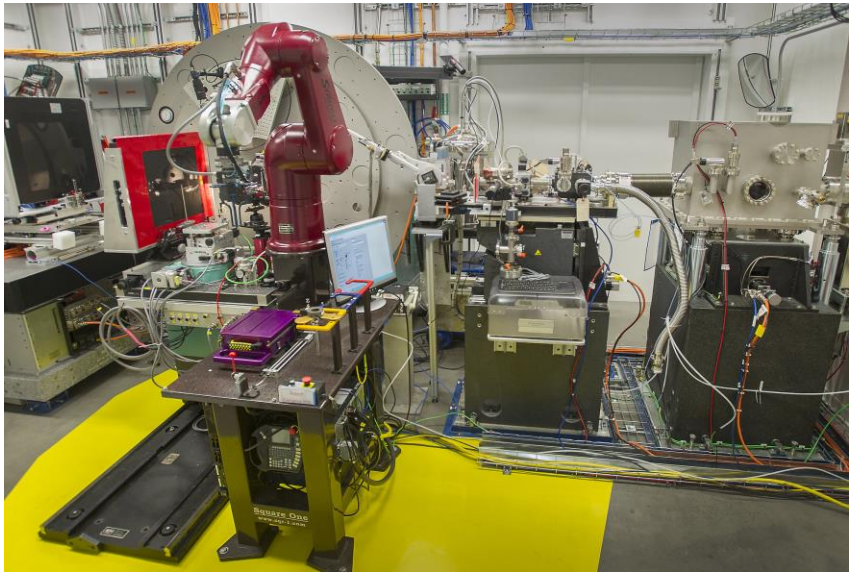
Month/Year	Milestones
Dec/2018	Complete *In situ* XRD studies of new low-cost P2-type iron based cathode materials ($Na_{0.7}[Cu_{0.15}Fe_{0.3}Mn_{0.55}]O_2$) for sodium-ion batteries during charge-discharge cycling. (Q1, December 2018) ➥ *Completed.*
Mar/2019	Complete the Synchrotron based XAS studies XAS analysis of $Na_{0.7}[Cu_{0.15}Fe_{0.3}Mn_{0.55}]O_2$ and $Na_{0.7}[Cu_{0.2}Fe_{0.2}Mn_{0.6}]O_2$ electrodes at different SOCs at Fe K-edge, Cu K-edge and Mn K-edge. (Q2, March 2019) ➥ *Completed.*
Jun/2019	Complete the soft x-ray absorption (sXAS) studies of $Na_{0.7}[Cu_{0.15}Fe_{0.3}Mn_{0.55}]O_2$ and $Na_{0.7}[Cu_{0.2}Fe_{0.2}Mn_{0.6}]O_2$ electrodes at different SOCs at Fe L-edge, Cu L-edge, and O K-edge.. (Q3, June 2019) ➥*On schedule.*
Sep/2019	Complete *In situ* XRD studies of new stabilized global P2 phase cathode material ($Na_{0.72}[Li_{0.24}Mn_{0.76}]O_2$)for sodium-ion batteries during charge-discharge cycling. (Q4, September 2019) ➥ *On schedule.*

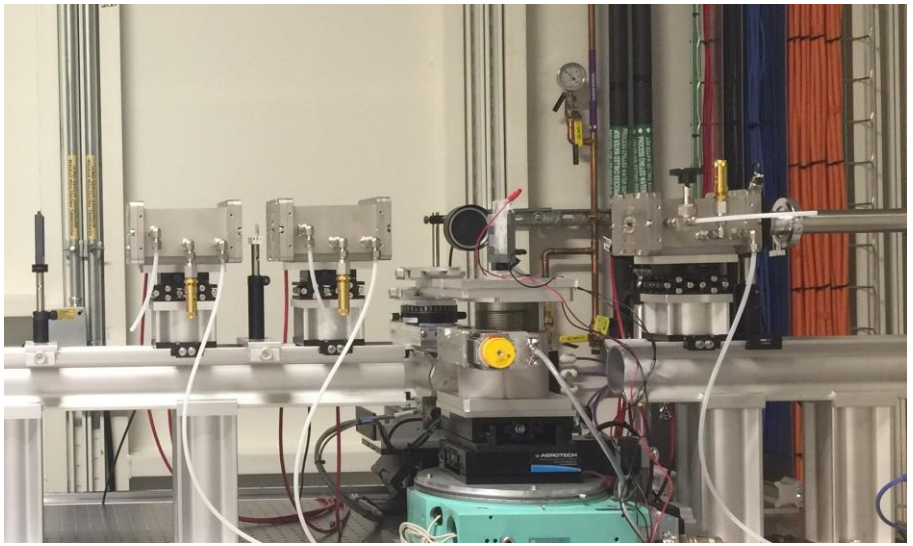
Approaches

- Synchrotron based X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS), to elucidate and differentiate the contribution from each component and element to the capacity and structural changes of various cathode and anode materials for Na-ion batteries.

- Extended collaboration with other US and international academic institutions and US industrial partners.

In situ X-ray diffraction and absorption beamlines at NSLSII





The photo of X-ray Powder Diffraction, or XPD beamline (left) and Quick X-ray Absorption and Scattering, or QAS beamline (right) at NSLSII for in situ/ex situ studies of Na-ion and Na-metal battery electrode materials.

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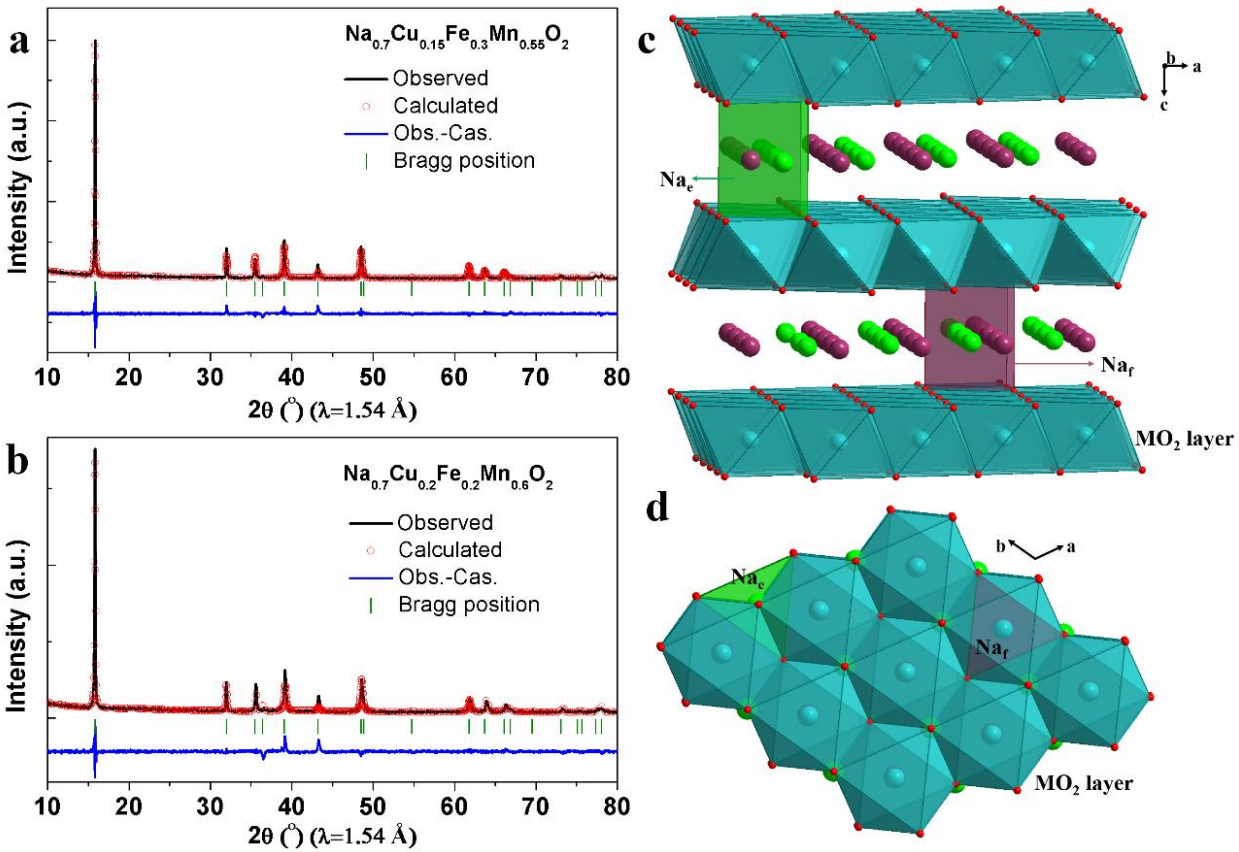
Technical Accomplishments

- Through collaboration with Prof. Yongning Zhou at Fudan University, Mg substituted P2-type $Na_{0.66}[Mn_{0.6}Ni_{0.4}]O_2$ as a new cathode materials for sodium ion batteries has been studied using synchrotron based XRD and XAS, the results was published on *Journal of American Chemistry Society (JACS)*.
- Through collaboration with Dr. Bohang Song, Dr. Jue Liu, and Dr. Katharine Page at Oak Ridge national Laboratory (ORNL), a novel P3-type $Na_{2/3}Mg_{1/3}Mn_{2/3}O_2$ as high capacity sodium-ion cathode with reversible contribution of oxygen redox reaction has been studied using ex situ X-ray absorption near edge spectroscopy (XANES) and Extended X-ray absorption find structure spectroscopy (EXAFS). The results of this study was published on *Journal of Material Chemistry A (JMCA)*.
- Through collaboration with Dr. Jue Liu at Oakridge National Laboratory and Prof. Peter Khalifah at Stony Brook University, $Na_3VP_3O_9N$ as a high-voltage cathode for rechargeable sodium ion batteries were studied. The results were published on *Chemistry Materials.*
- Through collaboration with Prof. Yongsheng Hu at Institute of Physics, Chinese Academy of Sciences, and Dr. Wanli Yang at Lawrence Berkeley National Laboratory (LBNL), New approaches to suppress the voltage decay of low-cost P2-type iron-based cathode materials for sodium-ion batteries were studied and the results were published on *Journal of Material Chemistry A (JMCA)*.

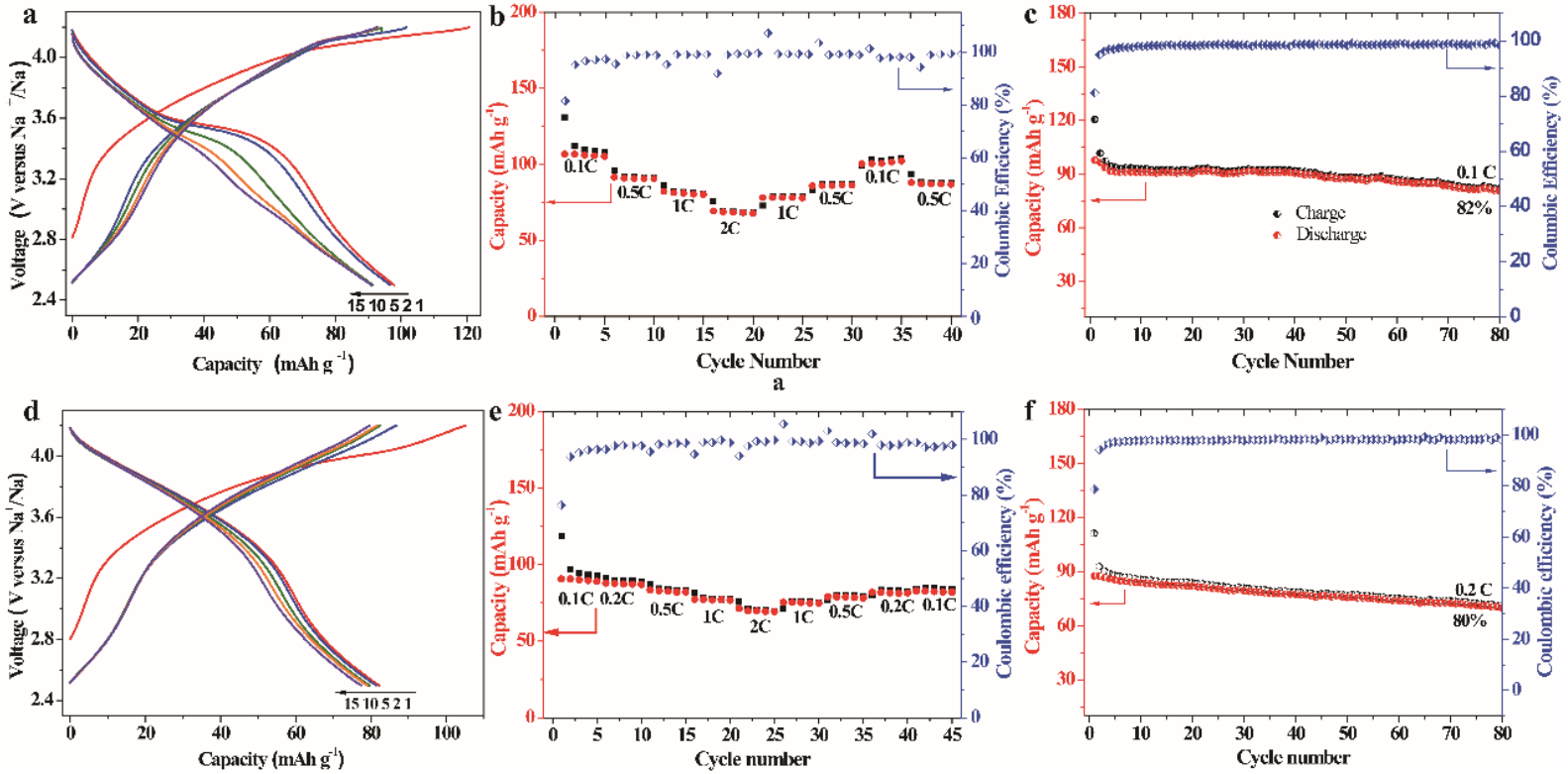
Structural Study of the Pristine NaCuFeMnO cathode Material



Structure of $Na_{0.7}[Cu_xFe_yMn_{1-x-y}]O_2$. X-ray diffraction patterns and Rietveld refinements of the as-prepared **a)** $Na_{0.7}[Cu_{0.15}Fe_{0.30}Mn_{0.55}]O_2$ and **b)** $Na_{0.7}[Cu_{0.20}Fe_{0.20}Mn_{0.60}]O_2$samples. The black (red) line represents the experimental (calculated) data. The residual discrepancy is shown in blue. Schematic illustration of the P2-typed layered structure viewed along **c)** the [010] direction and **d)** the [001] direction.

S. Xu, X.-Q. Yang, E. Hu, Y.-S. Hu et al., J. Mater. Chem. A, 2018, 6, 20795

Electrochemical Characterization of the NaCuFeMnO cathode Material



Electrochemical performance of the $Na_{0.7}[Cu_xFe_yMn_{1-x-y}]O_2$ electrodes. The galvanostatic charge and discharge profiles of **a)** $Na_{0.7}[Cu_{0.15}Fe_{0.3}Mn_{0.55}]O_2$ and **d)** $Na_{0.7}[Cu_{0.2}Fe_{0.2}Mn_{0.6}]O_2$ electrodes cycled between 2.5 and 4.2 V at a current rate of C/10. Note that the discharge capacity was normalized by the first discharge capacity. Rate capability of **b)** $Na_{0.7}[Cu_{0.15}Fe_{0.3}Mn_{0.55}]O_2$ and **e)** $Na_{0.7}[Cu_{0.2}Fe_{0.2}Mn_{0.6}]O_2$. The capacity versus cycle number at various current rates from C/10 to 2C. Long-term cycling performance of **c)** $Na_{0.7}[Cu_{0.15}Fe_{0.3}Mn_{0.55}]O_2$ and **f)** $Na_{0.7}[Cu_{0.2}Fe_{0.2}Mn_{0.6}]O_2$.

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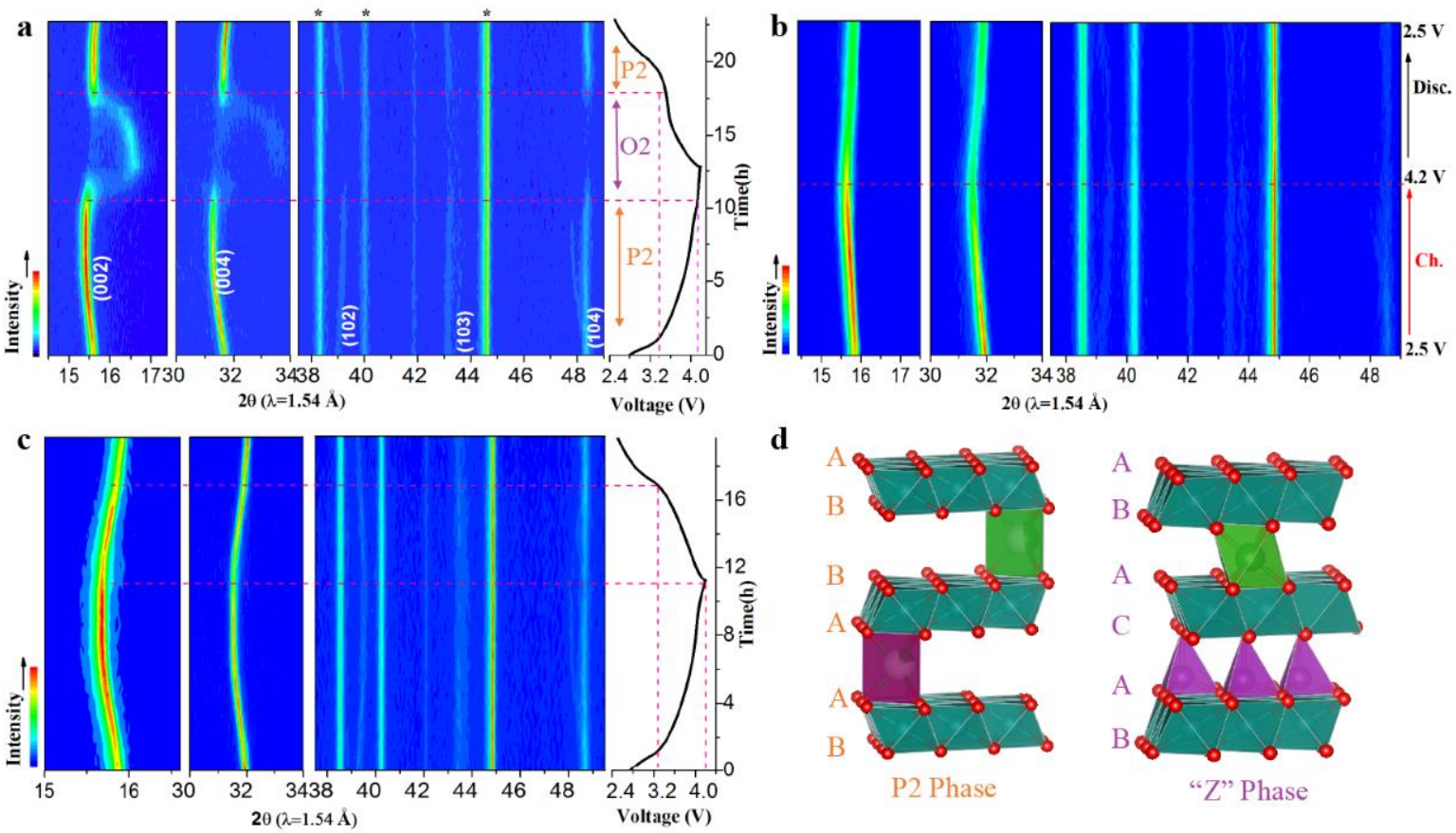
Global Structural Evolution of NaCuFeMnO Studied by in situ XRD



Structure evolution during Na extraction and insertion. *In situ* XRD patterns of $Na_{0.7}[Cu_{0.15}Fe_{0.3}Mn_{0.55}]O_2$electrode collected during **a**) the first and **b**) the fifth charge/discharge process. **c**) *In situ* XRD patterns of $Na_{0.7}[Cu_{0.2}Fe_{0.2}Mn_{0.6}]O_2$electrode collected during the first charge/discharge. All cycled between 2.5 and 4.2 V under a current rate of C/15. Black asterisks represent peaks from Al window. **d**) The scheme illustrations of the corresponding P2 phase and "Z" phase with O2 stacking viewed along the [100] direction.

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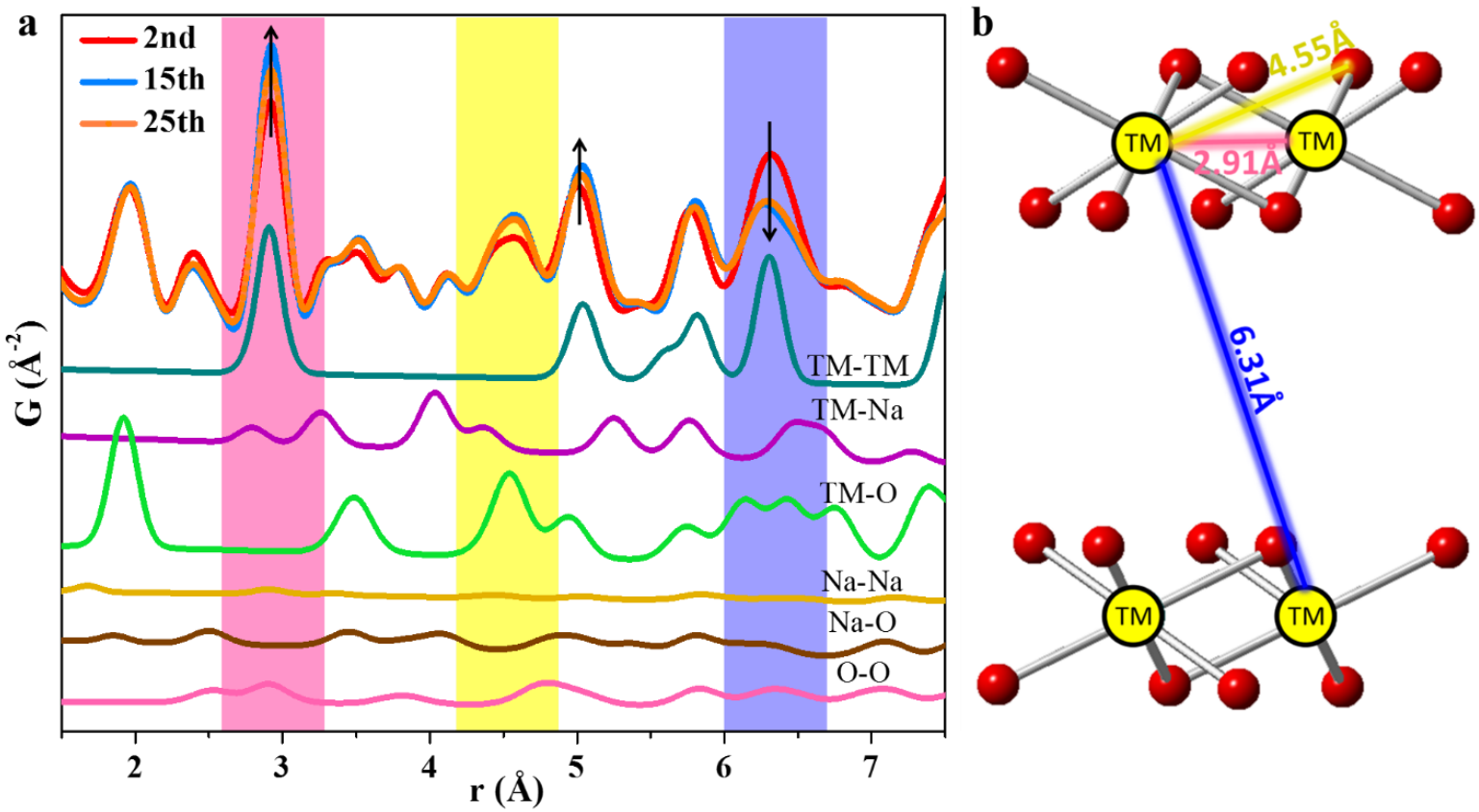
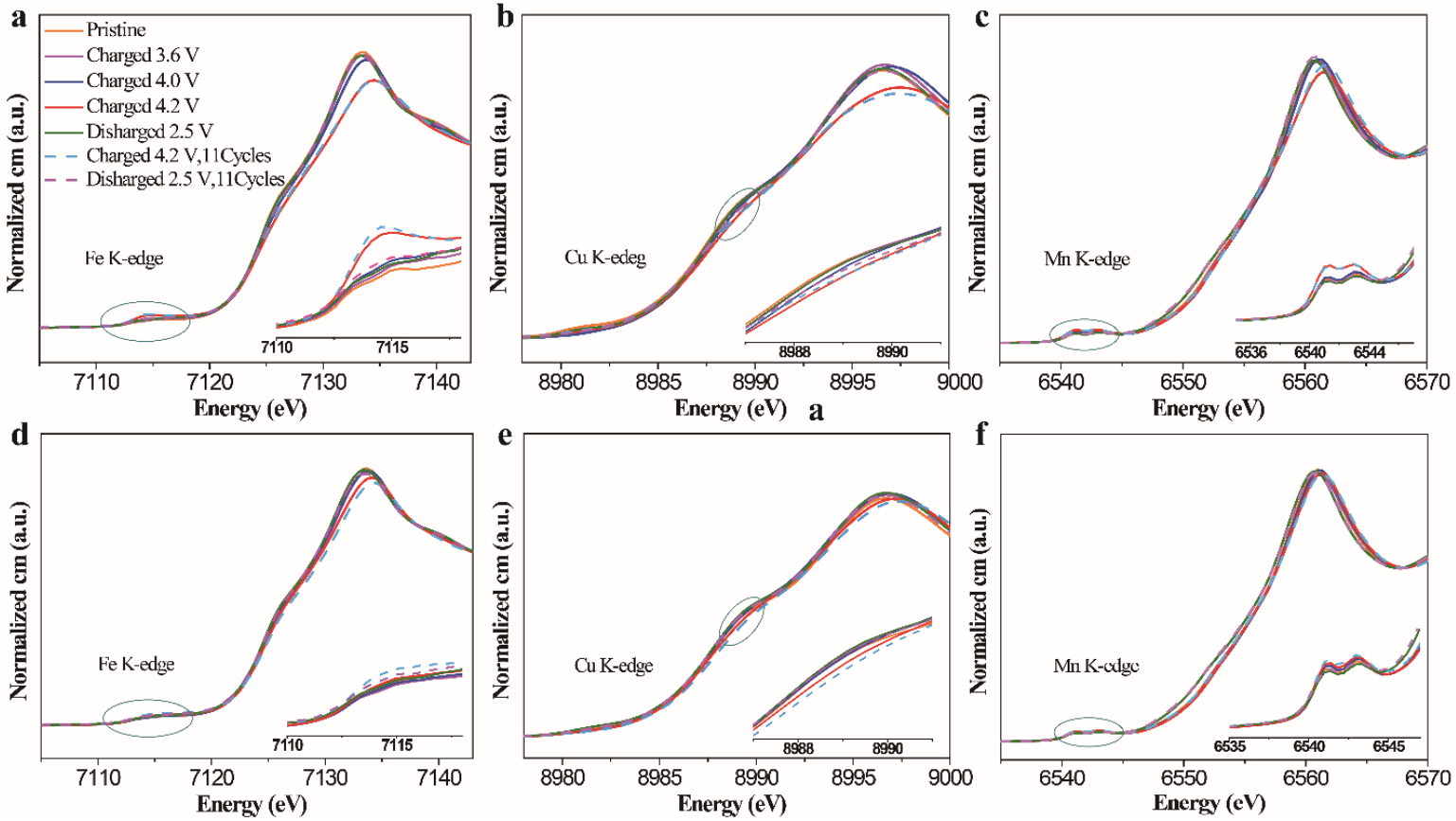
Local Structural Evolution of NaCuFeMnO Studied by ex situ PDF



Structure evolution during cycling. Comparison of the experimental PDF data of $Na_{0.7}[Cu_{0.15}Fe_{0.3}Mn_{0.55}]O_2$ with different charge-discharge cycles. First neighbor intralayer TM–TM and second neighbor intralayer TM–O distances in-plane are highlighted in lavender and yellow respectively, and interlayer TM–TM distances are highlighted in light purple. Scheme illustrations of the corresponding bond distances are also displayed with the same color.

S. Xu, X.-Q. Yang, E. Hu, Y.-S. Hu et al., J. Mater. Chem. A, 2018, 6, 20795

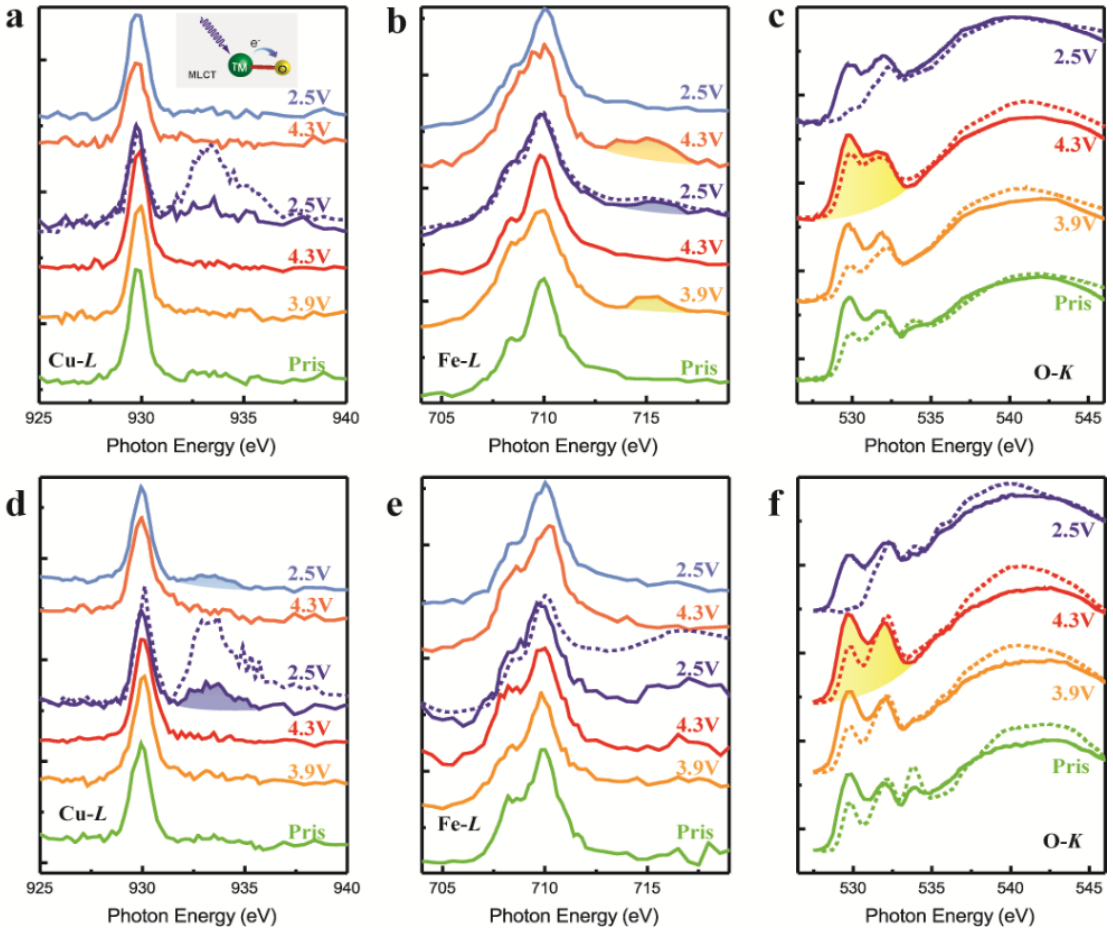
Charge Compensation Mechanism of NaCuFeMnO Studied by hXAS



XAS analysis of **a-c)** $Na_{0.7}[Cu_{0.15}Fe_{0.3}Mn_{0.55}]O_2$ and **d-f)** $Na_{0.7}[Cu_{0.2}Fe_{0.2}Mn_{0.6}]O_2$ electrodes at different SOCs during the 1st and 11th cycle: XANES spectra at **a), d)** Fe K-edge, **b), e)**Cu K-edge and **c), f)** Mn K-edge.

S. Xu, X.-Q. Yang, E. Hu, Y.-S. Hu et al., J. Mater. Chem. A, 2018, 6, 20795

Charge Compensation Mechanism of NaCuFeMnO Studied by sXAS



sXAS of $Na_{0.7}[Cu_{0.15}Fe_{0.30}Mn_{0.55}]O_2$ **(a-c)** and $Na_{0.7}[Cu_{0.20}Fe_{0.20}Mn_{0.60}]O_2$ **(d-f)** samples. For Cu L-edge (a), (d) and Fe L-edge (b), (e), and O K-edge (c), (f) sXAS, $Na_{0.7}[Cu_xFe_yMn_{1-x-y}]O_2$ cathode are collected at different cycle states, including the pristine, charge 3.9 V, charge 4.3 V, discharge 2.5 V during the very first cycle, as well as charge 4.3 V and discharge 2.5V during the 15th cycle. The spectra in solid lines are collected in TFY mode, while the dotted line demonstrates sXAS collected in TEY mode. Schematic diagram of metal to ligand charge transfer (MLCT) is shown in the inset of (a). The spectra evolution is highlight with shaded areas.

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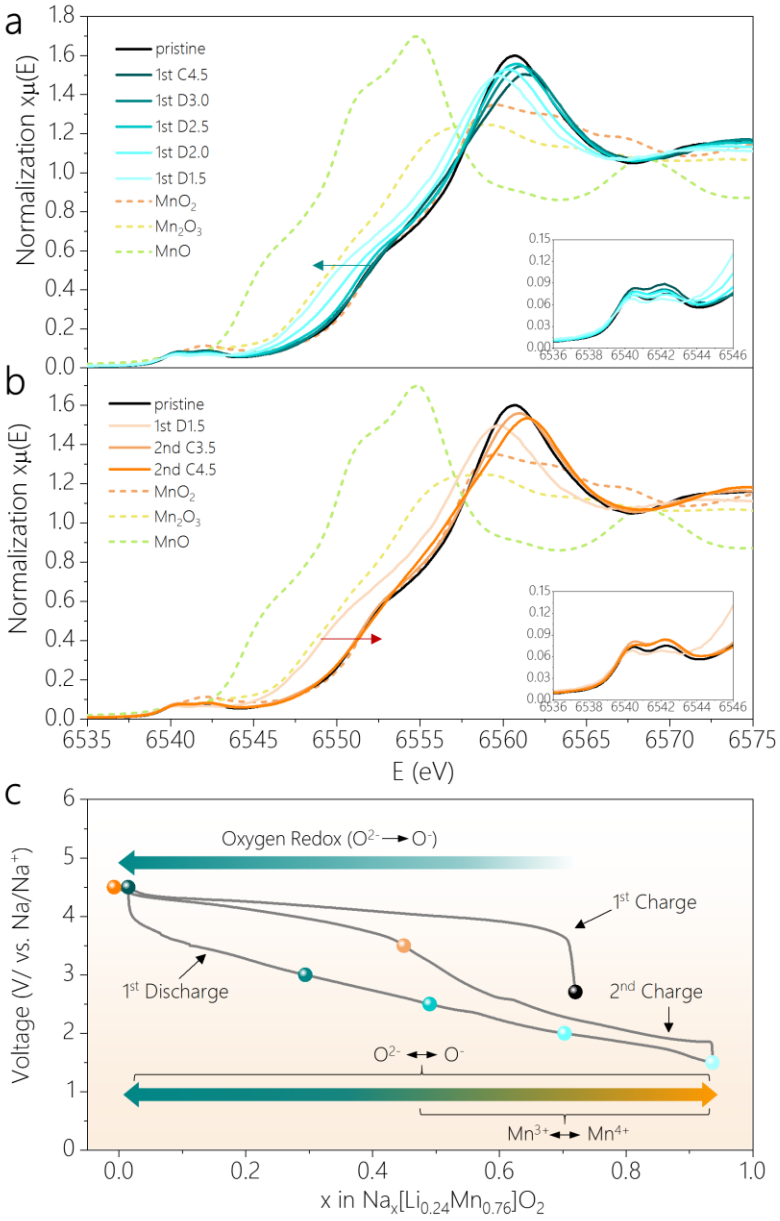
Charge Compensation Mechanism of NaLiMnO Studied by hXAS



Investigation of Charge Compensation Mechanism of $Na_{0.72}[Li_{0.24}Mn_{0.76}]O_2$ during Sodium Deintercalation-Intercalation (a and b) Normalized Mn K-edge XANES spectra of P2-type $Na_{0.72}[Li_{0.24}Mn_{0.76}]O_2$ electrode during charge and discharge of the initial cycle (a) and then during recharge to 4.5 V in the second cycle (b). (c) Function of sodium content and voltage. The chosen samples are marked with circles corresponding to colors in (a) and (b).

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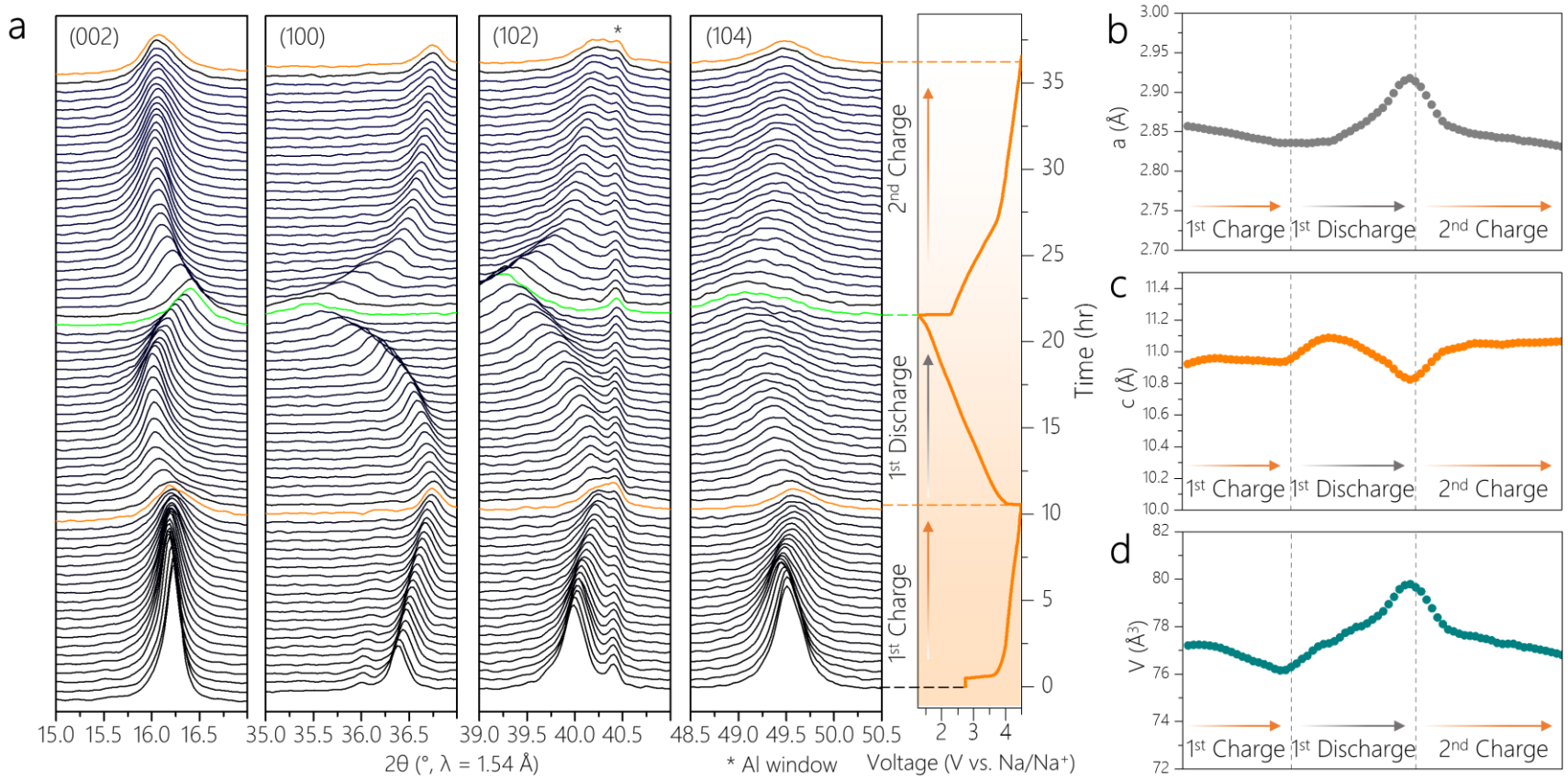
Global Structural Evolution of NaLiMnO Studied by in situ XRD



Crystal Structural Evolution of $Na_{0.72}[Li_{0.24}Mn_{0.76}]O_2$ Electrodes (a) In situ XRD patterns collected during the first charge/discharge and the second charge of the $Na_{0.72}[Li_{0.24}Mn_{0.76}]O_2$. (b–d) Evolution of the lattice parameters during the charge/discharge process: a axis (c), c axis (c), and unit cell volume (d).

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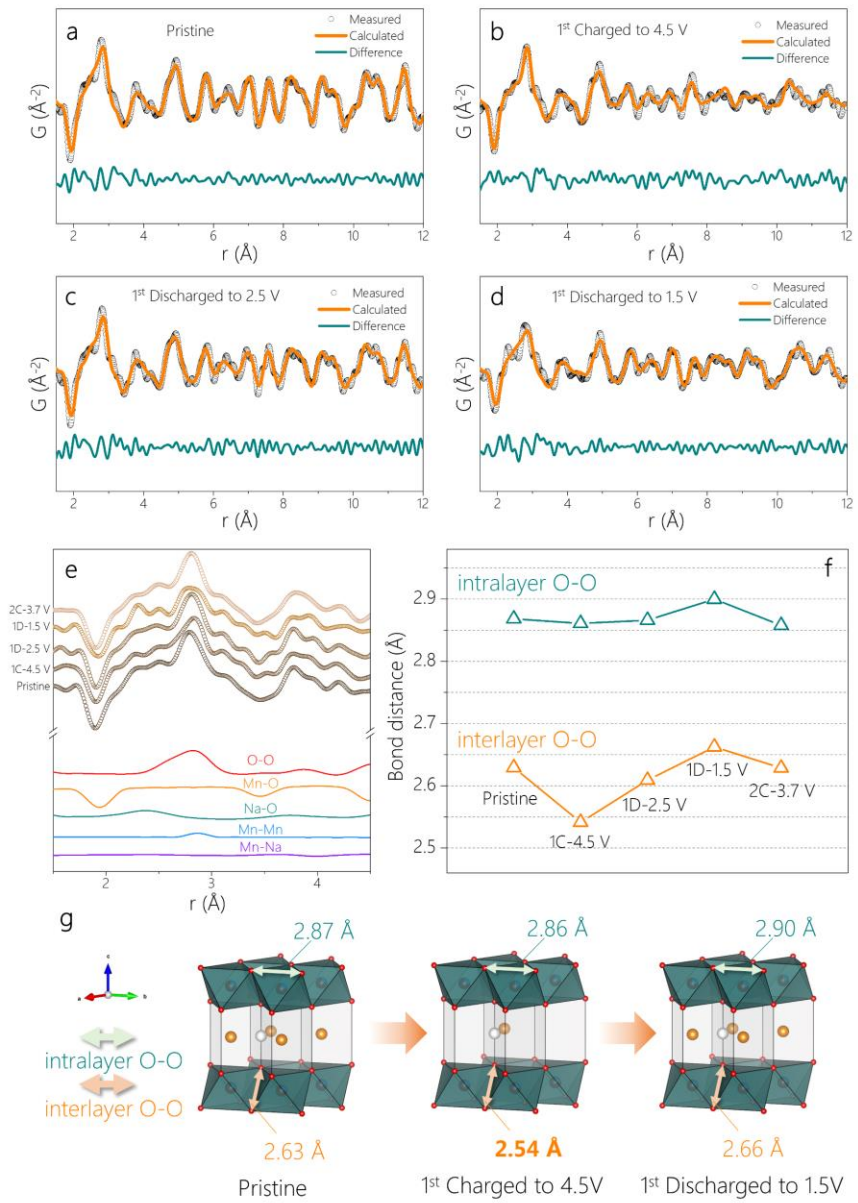
Local Structural Evolution of NaLiMnO Studied by neutron PDF



Detection of Local Structural Changes upon Deintercalation (a–d) neutron PDF of $Na_{0.72}[Li_{0.24}Mn_{0.76}]O_2$ collected at different states: pristine state (a), first charged to 4.5 V (b), first discharged to 2.5 V (c), and first discharged to 1.5 V (d). (e) Ex situ neutron PDF with contributions from major atomic pairs shown. (f and g) Evolution of O-O bond distance

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Response to last year reviewer's comments

Comments from 2017 AMR	Response
N/A	N/A

Collaborations with other institutions and companies

- **Lawrence Berkeley National Laboratory**
  Sodiation Kinetics of Metal Oxide Conversion
- **University of Maryland at College Park**
  Sodiation Kinetics of Metal Oxide Conversion
- **Drexel University**
  Probing the mechanism of high capacitance sodium anode materials in 2D titanium carbides
- **University of Texas-Austin**
  Removal of interstitial H_2O in hexacyanometallates for a superior sodium battery cathode
- **Massachusetts Institute of Technology (MIT)**
  A quaternary layered cathode compound for rechargeable Na ion batteries
- **Institute of Chemistry, Chinese Academy of Sciences**
  In situ XRD and XAS study of cathode materials for sodium batteries
- **Institute of Physics, Chinese Academy of Sciences**
  Studies on new cathode and anode material for sodium batteries using in situ XRD and XAS
- **Fudan University, Shanghai, China**
  In situ XRD and XAS study of cathode materials for sodium batteries

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Remaining Challenges and Barriers

- N/A

Proposed Future Work for *FY 2019* and *FY2020*

▣ **FY2019 Q3 Milestone:**

Complete the synchrotron based in situ x-ray diffraction studies of $Na_{0.66}Mn_{0.6}Ni_{0.2}Mg_{0.2}O_2$ as new cathode material for Na-ion batteries during charge-discharge cycling.

▣ **FY2019 Q4 Milestone:**

Complete the synchrotron based X-ray absorption near edge structure (XANES) studies of $Na_{0.66}Mn_{0.6}Ni_{0.2}Mg_{0.2}O_2$ as new cathode material for Na-ion batteries during charge-discharge cycling.

FY2020 work proposed:

- ▣ **Synchrotron based XRD and XAS, as well as pair distribution function (PDF) techniques will be applied to study the new cathode material $Na_{0.72}[Li_{0.24}Mn_{0.76}]O_2$ utilizing anionic redox reaction for Na-ion batteries.**
- ▣ **Neutron diffraction and (ND) and neutron pair distribution function (n-PDF) techniques will be applied to study the new cathode material $Na_{0.72}[Li_{0.24}Mn_{0.76}]O_2$ utilizing anionic redox reaction for Na-ion batteries.**
- ▣ **The collaborative research with US academic research institutions and industrial partners will be further expanded and strengthened.**

Summary

Relevance

- ✓ *To increase the energy density, searching for new cathode materials for Na-ion batteries.*
- ✓ *Diagnostics study aimed to improve the calendar and cycle life of batteries.*
- ✓ *Diagnostics study of new electrode materials with lower cost potential.*

Approaches

- *In situ x-ray diffraction and absorption spectroscopy*
- *Synchrotron based x-ray pair distribution function (XPDF)*
- *Neutro diffraction (ND) and neutron pair distribution function (n-PDF)*
- *Full field as well as micro- and nano- probe scanning TXM*
- *High resolution transmission electron microscopy (HR-TEM)*

Technical Accomplishments

- *$NaCrS_2$ as a anionic redox cathode material for sodium ion batteries has been studied using XRD and XAS.*
- *air-stable O3-Type cathode materials $NaNi_{0.45}Cu_{0.05}Mn_{0.4}Ti_{0.1}O_2$ as cathode materials for Na-ion batteries has been studied using synchrotron based XANES and EXAFS.*
- *Honeycomb ordered $Na_3Ni_{1.5}M_{0.5}BiO_6$ (M = Ni, Cu, Mg, Zn) as high voltage layered cathodes for sodium-Ion batteries has been studied*

Proposed Future work

- *Continue and complete the XAS and XRD studies of $Na_{0.66}Mn_{0.6}N_{i0.2}Mg_{0.2}O_2$*
- *Synchrotron based XRD and XAS, as well as pair distribution function (PDF) techniques will be applied to study the new cathode material $Na_{0.72}[Li_{0.24}Mn_{0.76}]O_2$ utilizing anionic redox reaction for Na-ion batteries*
- *Develop and apply the neutron diffraction (ND) and neutron PDF techniques for sodium battery material studies*